

G1. Ion Molecule Dissociation at High Pressure: Experiment and SACM/CT Calculations

A.A. Viggiano^a, *Abel. Fernandez^a*, *V.G. Ushakov^b*, *J. Troe^b*

^a Air Force Research Laboratory / VSBXT, 29 Randolph Rd., Hanscom AFB, MA 01731

E-mail: albert.viggiano@hanscom.af.mil

^b Institute for Physical Chemistry, University of Goettingen, Tammannstrasse 6, D37077 Goettingen, Germany

There are a number of moderately high-pressure plasmas that exist in the natural atmosphere, surrounding vehicles re-entering the atmosphere, plasma-enhanced combustion, and atmospheric discharges. In order to gain insight into pressure effects on reactivity, we have developed a turbulent ion flow tube to study ion reactivity at pressures up to an atmosphere and temperatures between 300 and 800 K. Here we report temperature and pressure effects on rate constants and branching ratios for a series of charge transfer reactions from O_2^+ to alkylbenzenes. The branching between dissociative and non-dissociative charge transfer clearly depends on both pressure and temperature. Increasing pressure at moderate temperature leads to more non-dissociative charge transfer since the lifetime of the excited alkylbenzene cation is long enough for buffer stabilization to occur. In contrast, higher temperature causes more dissociation in two ways: 1) the energy after charge transfer increases due to the thermal energy and 2) stabilized complexes thermally dissociate. Thus, whether the buffer stabilizes or dissociates the alkylbenzene cation depends critically on conditions, which shows the need for measurements over wide ranges.

The results are modelled by statistical adiabatic channel model – classical trajectory calculations (SACM/CT), where the SACM treatment is used for conserved modes and the trajectory calculations are used for transitional modes. Detailed and highly simplified, but still realistic, versions of SACM/CT are employed. Model potentials are formed by fitting to $k(E)$ results measured separately. Fitting the experimental $k(E)$ shows that accurate bond strengths can be derived by this technique, i.e. the fits can be extrapolated well outside the data range. The calculations are used to predict the TIFT pressure and temperature dependences using self-consistent calculations for high energy and thermal dissociation. From those calculations the amount of energy transferred per collision from the excited alkylbenzene ion to the buffer is derived. In addition, kinetic energy release distributions and kinetic shifts are calculated. The results are compared to those from RRKM models. Significant differences are found.

G2. On the Control of Product Yields in the Photofragmentation of Deuterium Chloride Ions (DCI^+) – The Relevance of Absolute Phase

*H. Georg Breunig^{a)}, Alexandra Lauer^{a)}, Mikhail V. Korolkov^{a,b)}, and
Karl-Michael Weitzel^{a)}*

^{a)} Philipps Universität Marburg, Fachbereich Chemie, Hans Meerwein Str., 35032 Marburg, Germany E-mail: weitzel@chemie.uni-marburg.de

^{b)} Stephanov Institute of Physics, National Academy of Science, Scarina ave.70, 220602 Minsk, Republic of Belarus

The enormous technical development of recent years has enabled not only valuable progress in understanding chemical dynamics but has also triggered efforts for controlling chemical reactions. Understanding such control schemes requires knowledge of all molecular quantum states involved. In the current work, we investigate hydrogen chloride ions (HCl^+ and DCI^+) for which a wealth of theoretical electronic structure data [1] and experimental spectroscopic data [2] is available. The relevant electronic states of the DCI^+ ion are presented in fig. 1.

We have investigated the prospect of controlling the photofragmentation of deuterium chloride ions (DCI^+) via strong ultra short IR laser pulses by numerical solution of coupled Schrödinger equations. The calculations provide evidence that the ratio of product ion yields Cl^+ versus D^+ can be manipulated by appropriate choice of laser pulse parameters, in particular central laser wavelength, pulse duration, intensity and chirp [3]. For example, laser pulses with negative chirp are predicted to form 95% Cl^+ at 1865 cm^{-1} , but $> 80\%$ D^+ at 1550 cm^{-1} (see fig. 2). The analysis of time dependent populations reveals competition between intra- and inter-electronic state excitation, enabling the understanding of quantum control at the molecular level. The absolute phase of the laser field turns out to be crucial for the photofragmentation dynamics, since the interaction between different electronic states is phase sensitive. First experiments attempting to confirm these calculations by employing fs laser pulses will be presented.

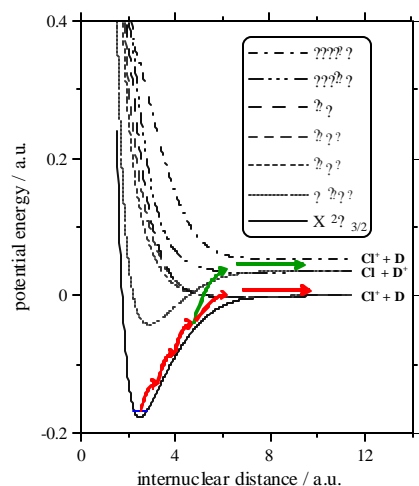


Fig. 1 Potential energy diagram of relevant electronic states in DCI⁺ with dissociation limits.

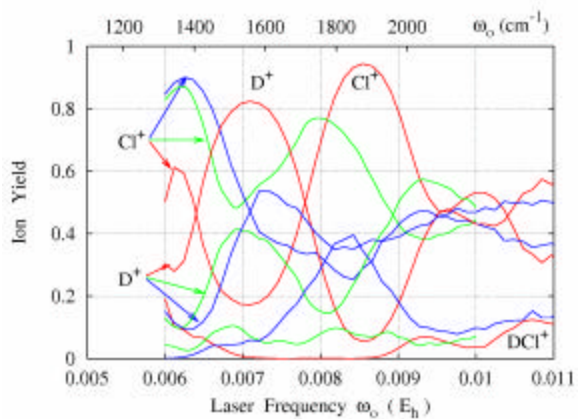


Fig. 2 Relative product ion yield as a function of the laser frequency: blue = up chirp, green = no chirp, red = down chirp.

Reference:

- [1] A.D. Pradhan, K.P. Kirby, A. Dalgarno, J. Chem. Phys., 95, 9009, (1991).
- [2] M. Michel, M.V. Korolkov, K.-M. Weitzel, J. Phys. Chem. A, 108, 9924, (2004).
- [3] M.V. Korolkov, K.-M. Weitzel, to be published in J. Chem. Phys.

G3. High-Temperature Ion-Molecule Kinetics Measurements by a Novel Technique: The Reactions of Ca^+ with N_2O and O_2

Biljana Cosic^a, Alexandre Ermoline, and Arthur Fontijn

High-Temperature Reaction-Kinetics Laboratory, Isermann Department of Chemical and Biological Engineering, Rensselaer Polytechnic Institute,
110 - 8th Street, Troy, N.Y. 12180-3590

a)Present address: Dept. of Chemistry, University of Waterloo, Waterloo, Ontario, Canada

E-mail: bcosic@sciborg.uwaterloo.ca, ermola@rpi.edu, fontia@rpi.edu

Ion-molecule reactions are of current combustion, ionospheric, and theoretical interest. For combustion, metal cations are of importance, as these, due to their low-ionization potentials, rapidly can become the major charge carriers even when present in small concentrations. The lifetime of the charged species applications depends critically on whether the metals are present as atoms or as molecular ions. However, kinetic data for metallic species at combustion temperatures are very rare. Earlier work has generally been done at or near room temperature or in beam-gas apparatus, where effective temperatures, different from kinetic (Boltzmann) temperatures, are calculated.

In previous work we have developed thermostatted reactors for the study of isolated elementary reactions of neutral species in the 300 - 1800 K range [1]. We have now modified one of these apparatus types, the slow-flow pseudo-static HTP (high-temperature photochemistry) reactor, for similar studies of metal cations, Fig. 1. In the experiments done thus far Ca^+ was produced by multiphoton (193 nm) photolysis of calcium acetyl acetonate. The $[\text{Ca}^+]$ was monitored by LIF at 393.4 nm in essentially the same volume element as in which it was formed. Total pressures, mainly of bath gas Ar, were in the 50-800 mbar range.

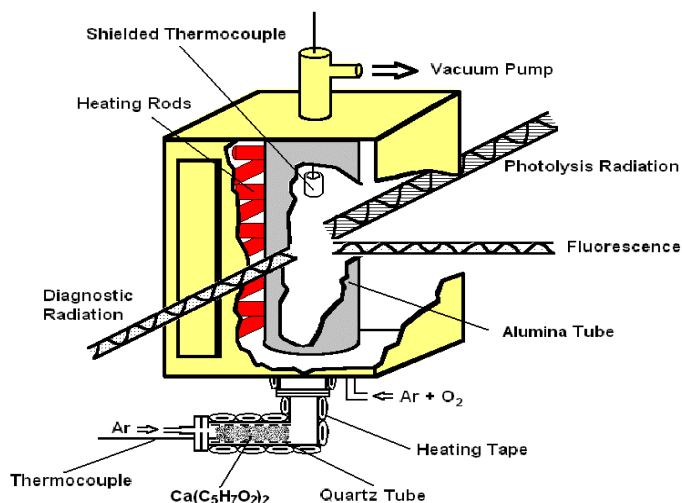


Fig.1: The modified HTP apparatus

For $\text{Ca}^+ + \text{N}_2\text{O} \rightarrow \text{CaO}^+ + \text{N}_2$
we obtained k (478 - 1207 K) = $1.7 \times 10^{-10} \exp(-150 \text{ K/T}) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. This reaction has simultaneously been studied from 188-371 K by J.M.C. Plane's group, at the University of East Anglia. Extrapolation of our best-fit line is in excellent agreement with their $T > 275 \text{ K}$ data. At lower temperatures a change in mechanism occurs and the k -values increase with decreasing temperatures.

For $\text{Ca}^+ + \text{O}_2 + \text{Ar} \rightarrow \text{CaO}_2^+ + \text{Ar}$
we measured k (910 - 1430 K) = $3.3 \times 10^{-32} \exp(+3260 \text{ K/T}) \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$. These data, the temperature range of which is to be extended, correspond to a $T^{-2.8}$ dependence. This dependence is comparable to that of the $T < 300 \text{ K}$ observations on Na^+ association reactions by flow tube-mass spectrometric techniques [2,3].

In the presentation the results will be compared to the N_2O and O_2 reactions of the iso-electronic neutral species K, as well as of Ca.

Work supported by NSF grant CTS - 0224778

References

1. A. Fontijn and P.M. Futerko, in *Gas Phase Metal Reactions* A. Fontijn, Ed., North-Holland, 1992, Chap. 6.
2. R.M. Cox and J.M.C. Plane, *J.C.S. Faraday Trans.* 93, 2619 (1997).
3. R. Passarella and A.W. Castleman, Jr., *J.Phys. Chem.* 93, 5840 (1989).